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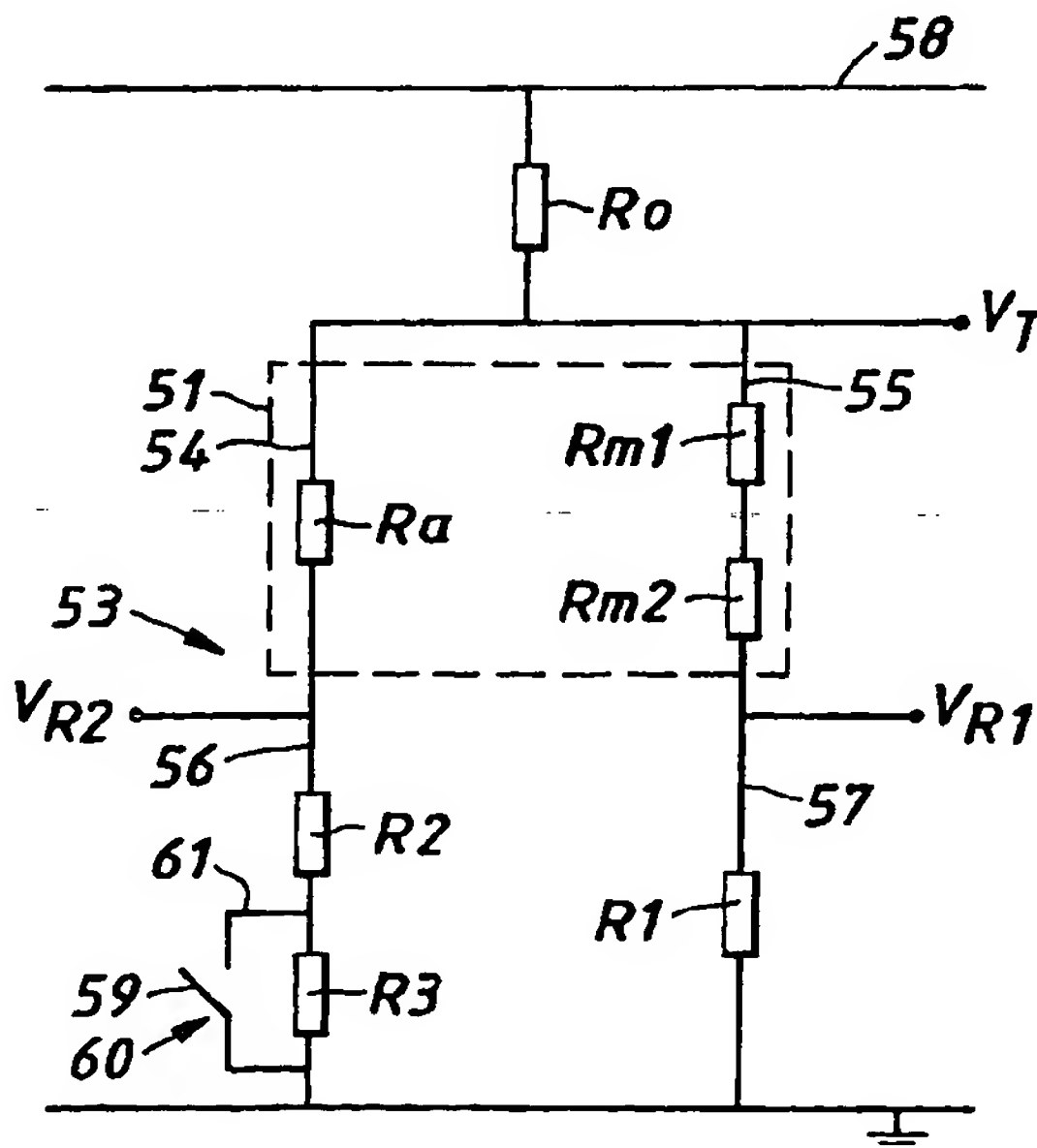
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(54) Title: MEASUREMENT OF FLUID CONCENTRATIONS

(57) Abstract

An apparatus and method for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas (LNG). The percentage of methane or ethane/methane ratio of the LNG is determined by measuring the thermal conductivity of the LNG at two temperatures.



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MEASUREMENT OF FLUID CONCENTRATIONS

The present invention relates to the measurement of the concentration of one or more constituents of a fluid mixture, particularly liquid natural gas (LNG).

LNG is currently being used as an alternative clean fuel for large vehicles such as buses and trucks. The LNG production process removes the carbon dioxide, water and odourant present in natural gas and leaves essentially only methane, ethane, propane and butane.

Operational problems have been observed with LNG vehicles which are due to the gas composition in a vehicle's tank and fuel line changing with time as shown by the chromatographic analysis of bagged samples from "fresh" and "old" tank gases shown below:-

% volume	methane (CH ₄)	ethane (C ₂ H ₆)	propane (C ₃ H ₈)	butane (C ₄ H ₁₀)
"Fresh" LNG				
sample 1	98.24	1.51	0.20	0.05
sample 2	99.88	0.12	0.00	0.00
"Old" LNG				
sample 1	84.76	13.15	1.63	0.40
sample 2	83.10	14.31	2.01	0.49

The shift in the relative proportions of methane to non-methane components with time can be clearly seen.

This variation in LNG gas composition can affect the performance of the engine and may lead to damage through "knock". It has been proposed that this composition change is caused by preferential "boil off" of methane from the LNG mixture. Methane has a much lower boiling point than the other components as shown below:

	methane	ethane	propane	butane
boiling point °C	-161.5	-88.6	-42.1	-0.5

According to a first aspect of the present invention there is provided an apparatus for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas, the apparatus comprising means to measure the thermal conductivity of the mixture at two different temperatures and control means to determine the proportion of at least one of the components of the mixture from the thermal conductivity measurements.

Such an apparatus provides a precise determination of the proportion of at least one of the components of the LNG and with a suitable thermal conductivity sensor is robust, has a fast response time and is inexpensive to produce.

The apparatus may also have means to measure one or both of the temperature and pressure of the mixture. The control means would then be arranged to determine the proportion of at least one of the components of the mixture from the thermal conductivity

measurements and the respective one or both of the temperature and pressure measurements.

The proportion of at least one of the components that is determined may be the proportion of methane or the ethane/methane ratio.

The apparatus is preferably used with an engine management system to ensure appropriate operation of a liquid natural gas fuelled engine despite fluctuations in the proportion of components of liquid natural gas supplied to the engine.

According to a second aspect of the present invention there is provided a method for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas, the method comprising measuring the thermal conductivity of the mixture at a first temperature, measuring the thermal conductivity of the mixture at a second temperature and determining the proportion of at least one of the components of the mixture from the thermal conductivity measurements.

An example of the present invention is described below with reference to the accompanying drawings in which:

Figure 1 diagrammatically shows an apparatus to determine the proportion of at least one component of a fluid mixture of liquid natural gas flowing in a conduit;

Figure 2 is a flow diagram of the procedure followed by a control means in the apparatus of Figure 1;

Figure 3 is a graph showing the determined methane proportion of a number of mixtures plotted against the actual methane proportion of the mixtures;

Figure 4 is a graph showing the determined ethane/methane ratio of a number of mixtures plotted against the actual ethane/methane ratio of the mixtures;

Figure 5 diagrammatically shows a thermal conductivity sensor which may be used in the apparatus to determine the proportion of at least one component of an LNG mixture positioned in the cut away wall of a conduit;

Figure 6 diagrammatically shows an electrical circuit for operating a thermal conductivity sensor;

Figure 7 shows the sequence of operations for controlling a sensor; and

Figure 8 shows a thermal conductivity sensor characteristic.

The apparatus shown in Figure 1 comprises a control means 1 which may be a computer or a microprocessor for example connected to a thermal conductivity sensor 2, a temperature sensor 3, and an absolute pressure sensor 4 by connectors 5, 6 and 7 respectively. In this example the thermal conductivity sensor 2, temperature sensor 3 and pressure sensor 4 are mounted to and arranged to take measurements of the contents of a conduit arranged to transport LNG and which may be a fuel line for supplying LNG to an engine. The thermal conductivity sensor and temperature sensor may take any suitable form as are well known in the art. However, in a preferred example the thermal conductivity sensor 2 and temperature sensor 3 are combined in a single unit as described later. The absolute pressure sensor may take any suitable form such as an orifice plate or a by-pass venturi as are well known in the art.

When the proportion of methane or the ethane/methane ratio of the contents of the conduit 8 is to be determined the control means 1 follows the procedure shown in Figure 2. At step 21 the control means 1 instructs the thermal conductivity sensor 2 to take a thermal conductivity measurement of the contents of the conduit 8 at a first temperature and stores the result, ThC(St). At step 22 the control means 1 instructs the thermal conductivity sensor 2 to take a thermal conductivity measurement of the contents of the conduit 8 at a second temperature and stores the result ThC(R). For more precise results steps 21 and 22 may be repeated one or more times to obtain an average value for the thermal conductivity at each of the first and second temperatures. In the preferred example 5000 results are taken with a 1 second delay between each reading to provide time for the detector to settle to the measuring temperature.

At step 23 the control means 1 reads the ambient temperature T of the contents of the conduit 8 from the temperature sensor 3 and stores the result and at step 24 the control means 1 reads the absolute pressure P of the contents of the conduit 8 and stores the result.

At step 25, to determine the proportion of methane in the LNG mixture in the conduit 8 the control means 1 uses the values stored from steps 21-24 in the following relationship:

$$CH_4 = aP + bT + cT^2 + dThC(St) + eThC(R) + f \quad (1)$$

Where:

- CH₄ is the inferred methane percentage
- P is the absolute pressure of the fluid in the conduit
- T is the temperature of the fluid in the conduit
- ThC(St) is the thermal conductivity of the fluid in the conduit at a first temperature
- ThC(R) is the thermal conductivity of the fluid in the conduit at a second temperature

and a, b, c, d, e and f are constants determined from experimental data using linear regression.

When pressure is measured in units of bar A, temperature is measured in degrees Celsius and thermal conductivity is measured in units of Watts/metre x Kelvin (W/m.K). The constants a - f have substantially the following values:

a = -0.44, b = -0.39, c = 0.0017, d = 41, e = -42 and f = -181

Additionally or alternatively to step 25, at step 26 the ethane to methane ratio of the LNG mixture in the conduit 8 is determined using the values stored from steps 21-24 in the following relationship:

$$C2/C = gP + hT + iT^2 + jThC(St) + kThC(R) + l \quad (2)$$

where:

C2/C is the inferred ethane/methane ratio as a percentage and

g, h, i, j, k and l are constants determined from experimental data using linear regression.

When pressure is measured in units of bar A, temperature is measured in degrees Celsius and thermal conductivity is measured in units of Watts/metre x Kelvin (W/m.K) the constants g - l have substantially the following values:

g = 0.0053, h = 0.0051, i = -0.000024, j = -0.61, k = 0.66 and l = 3.14.

Either or both of the determined values of inferred methane percentage and inferred ethane/methane ratio may then be used by an engine management system. The engine management system could then ensure appropriate operation of an LNG fuelled engine despite fluctuations in the proportion of components of LNG supplied to the engine to achieve efficient operation. The engine management system could adjust the ignition timing in response to the LNG quality to stop the engine knocking. Alternatively or

additionally the profile for the throttle control could be altered depending upon the quality of the LNG, eg if the LNG is poor the throttle would have to be opened more to obtain the same power. Alternatively either or both of the inferred methane percentage and inferred ethane/methane ratio may be used for any suitable purpose or displayed.

The apparatus for determining the proportion of at least one of the components of a fluid mixture was tested on four gas mixtures shown below chosen to represent the variation from "fresh" to "old" LNG.

Test Gas	CH ₄	C ₂ H ₆	C ₃ H ₈	nC ₄
Sample 1	100.00	0.000	0.000	0.000
Sample 2	94.996	4.240	0.472	0.292
Sample 3	90.009	8.620	0.861	0.510
Sample 4	85.006	12.700	1.430	0.864

Although this test was performed with gaseous mixtures, the test was found to work equally well with liquid mixtures as in LNG.

The test apparatus comprised a thermal conductivity sensor arranged to measure the thermal conductivity at two temperatures, an absolute pressure sensor and a temperature sensor all positioned in an environmental cabinet into which the test gas samples were sequentially introduced. Each of the sensors was calibrated against standard instruments. The temperature of each sample was varied by the environmental chamber and the absolute pressure inside the chamber was varied using a precision regulator.

Figure 3 shows the determined or inferred methane percentage of each sample on the Y-axis and the actual methane percentage on the X-axis. The inferred values agree with the actual values very closely with only a very small error. Repeated experimental results using the above method were found to produce a range of two standard deviations within $\pm 0.33\%$ of the actual methane proportions. Thus using relationship No. 1 produced very precise data which would provide very efficient engine management.

Figure 4 is similar to Figure 3 except showing the inferred ethane/methane ratio on the Y-axis and actual ethane/methane ratio on the X-axis. Repeated experimental results using the above method were found to produce a range of two standard deviations within $\pm 0.0049\%$ of the actual ethane/methane ratio which was even more precise than for the inferred methane proportion shown in Figure 3 using relationship No. 1. Again, using relationship No. 2, very precise data is produced which can be used for efficient engine management.

Experiments performed using the environmental chamber indicated that pressure variations caused only a minor difference to the final calculated proportions. This suggests that the absolute pressure sensor could be omitted for less precise requirements such as a cheaper sensor.

The thermal conductivity of the LNG can be measured by any suitable device or method. However, the preferred method uses a sensor having a resistor arranged to be surrounded by the fluid being tested. For precise measurements, the resistor needs to be thermally isolated from the substrate upon which it is supported so that heat generated by the resistor is substantially only transferred away from the resistor by conduction through the surrounding fluid. The resistor may be heated to a temperature above ambient by applying electrical power to the resistor to measure the thermal conductivity of the fluid at that temperature. The preferred sensor also has an additional resistor for measuring

the ambient temperature. This resistor is thermally bonded to its substrate to ensure that it is maintained at ambient temperature. The effective resistances of the resistors are dependent upon their temperatures.

There is preferably provided a control circuit for a thermal conductivity sensor having a resistor arranged to be exposed to a fluid the thermal conductivity of which is to be determined, the control circuit comprising means to heat the resistor to at least two different temperatures and means arranged to provide a signal indicative of the thermal conductivity of the fluid at each of the at least two temperatures to which the resistor is heated. Such a control circuit is able to provide thermal conductivity measurements of a fluid at more than one temperature which is useful in the determination of the proportions of one or more of the constituents of LNG. Precise thermal conductivity measurements can be produced from such a sensor which is inexpensive, compact and robust. The control circuit may form part of the control means 1 described earlier.

Figure 5 diagrammatically shows a thermal conductivity sensor 51 as described above positioned in the wall of a gas pipe 52 with the thermal conductivity measuring resistor R_m and ambient temperature measuring resistor R_a exposed to the gas flowing inside the pipe. Of course the sensor 51 may be arranged to measure the thermal conductivity of any fluid whether it be flowing or static.

The resistance of these elements varies approximately with temperature according to the relationships:

$$(3) \quad \dots R_m = R_{m0} (1 + \alpha T_m)$$

$$(4) \quad \dots R_a = R_{a0} (1 + \alpha T_a)$$

Where:-

R_{m0} is the resistance of the thermal conductivity measuring resistor R_m at 0°C
(Nominally 200Ω for two in series)

R_{a0} is the resistance of the ambient temperature measuring resistor R_a at 0°C
(Nominally 235Ω)

α is the temperature coefficient of resistance of the material of the resistor
(nominally $5.5 \times 10^{-3}/\text{K}$).

T_m is the temperature of the heated thermal conductivity measuring resistor.

T_a is the temperature of the ambient temperature measuring resistor.

To enable the thermal conductivity of the gas surrounding the thermal conductivity measuring resistor R_m to be determined power must be applied to the resistor R_m by connecting it to a voltage source. From the temperature elevation and power applied the thermal conductivity of the gas surrounding the thermal conductivity measuring resistor R_m can be calculated using:-

$$(5) \quad \dots k = \Psi(P/\theta)$$

Where

k is the thermal conductivity of the gas (Typically $3.65 \times 10^{-5} \text{ W/K}$ for air at room temperature)

Ψ is a scaling constant related to the construction of the sensor (order of 0.0036)

- P is the power dissipated in the heated measuring resistor R_m and
 Ψ is the temperature of the heated measuring resistor R_m above ambient

The sensor 51 is shown in Figure 6 connected in a circuit 53 to control it so that thermal conductivity values for the gas flowing in the pipe 8 at a variety of temperatures can be determined.

The circuit 53 essentially consists of a bridge circuit having two arms 54, 55 connected to the supply voltage 58, in this case via current limiting resistor R_o and two arms 56, 57 connected to earth.

One of the arms 54 connected to the supply voltage 58 includes the ambient temperature measuring resistor R_a and the other arm 55 connected to the supply voltage 58 includes the thermal conductivity measuring resistor R_m , which in this example consists of two resistors R_{m1} , R_{m2} connected in series.

The arm 56 connected between arm 54 and earth has in this example two resistors R_2 , R_3 in series. R_3 can be short circuited when desired. Resistor R_3 can be short circuited by the appropriate control signal applied on line 59 to transistor 60 in path 61 parallel to resistor R_3 to close the path 61 and by-pass resistor R_3 . The final arm 57 of the bridge has a resistor R_1 . Resistors R_1 , R_2 and R_3 enable the current through the heated thermal conductivity measuring resistor R_m and the ambient temperature measuring resistor R_a to be determined. They also limit the current passing through the sensor during fault conditions preventing or reducing sensor damage.

The bridge circuit maintains $V_{R1} = V_{R2}$ so that the bridge is 'balanced' by adjusting the voltage V_T at the top of the bridge. This controls the effective resistance of the heated

measuring resistor R_m to be a constant multiple of the ambient temperature sensing resistor R_a given by the following relationship:

$$(6) \quad \dots R_m = R_a (R_1/R_2) \text{ when } R_3 \text{ is by-passed}$$

In the present example $R_1 = R_2$ (249Ω) so that

$$(7) \quad \dots R_m = R_a$$

This value of R_m corresponds to a temperature to which the thermal conductivity measuring resistor R_m is heated as determined by equation (3) which in the present example is approximately 80°C above ambient.

The thermal conductivity of the gas surrounding the thermal conductivity sensing resistor R_m at the temperature to which R_m is heated can then be determined using equation (5):

$$k = \Psi(P/\theta)$$

Since the temperature above ambient (θ) is known as it is fixed by R_1 and R_2 and since Ψ is a constant for a particular sensor, the thermal conductivity k at a particular temperature to which R_m is heated can be found by making a measure of the power (P) dissipated across R_m at that temperature.

The power P dissipated across R_m is given by:

$$(8) \quad \dots \text{Power} = I^2 R_m$$

Since the current passing through R_m is the same as that passing through R_1 , the current can be found by:

$$(9) \dots I = V_{R_1}/R_1$$

Therefore the power dissipated across the thermal conductivity measuring resistor is found to be:

$$(10) \dots \text{Power} = V_{R_1}^2 R_m / (R_1)^2$$

substituting equation (10) into equation (5) using equations (3) and (4) gives the following result as explained in the appendix:

$$(11) \dots k = \Psi V_{R_1}^2 \alpha R_{ao} R_{mo} / (R_{ao} - R_{mo}) R_1^2$$

As Ψ , α , R_{ao} , R_{mo} and R_1 are all constants the thermal conductivity k of the gas surrounding the thermal conductivity sensing resistor R_m is proportional to the square of the voltage across R_1 :

$$(12) \dots k \propto V_{R_1}^2$$

$$(13) \dots k = z V_{R_1}^2$$

The proportionality constant z will vary for each sensor manufactured due to resistor tolerances and so can be found by a separate calibration experiment using a gas of known thermal conductivity at the temperature to which R_m is heated. Hence the thermal conductivity of a gas surrounding resistor R_m at a first temperature can be determined directly from the square of the voltage across resistor R_1 using a first predetermined proportionality constant z .

To determine the thermal conductivity of the gas at a second temperature, resistor R3 (20Ω) is included in series with R2. This is achieved by the application of an appropriate control signal on line 59 to transistor 60 to open path 61. In order to maintain $V_{R1} = V_{R2}$ in the bridge circuit the voltage V_T is adjusted, changing the effective resistance of Rm which is given by:

$$(14) \quad \dots R_m = R_a (R_1 / (R_2 + R_3))$$

This different effective value of Rm makes it operate at a different temperature from that when R3 is by-passed. The temperature is defined by equation (3). When R3 is in series with R2, Rm is heated to approximately 60°C above ambient.

The thermal conductivity of the gas surrounding resistor Rm at this second temperature can then be found from the square of the voltage across R1 as before using equation (13). However, in this case the proportionality constant z will be different and can be found by a separate calibration experiment using a gas of known thermal conductivity at the second temperature.

Hence by including or excluding R3 in arm 56 of the bridge circuit the temperature to which Rm is heated can be controlled to be one of two substantially predetermined values and the thermal conductivity of the surrounding gas can be determined at those two temperatures using predetermined constants. Of course more resistors can be controlled to be included or excluded in arm 6 of the bridge circuit to be able to determine the thermal conductivity of the surrounding gas at even more temperatures.

The temperatures to which the thermal conductivity measuring resistor Rm is heated are determined by the values of R1, R2 and R3 as shown by equations (3), (6) and (14). In

the present example when R3 is by-passed, Rm is heated to approximately 80°C above ambient and when R3 is not by-passed Rm is heated to approximately 60°C above ambient.

However, a possible side effect of the circuit design is that the temperatures to which resistor Rm is heated and thus the temperatures at which the thermal conductivity is measured are dependent upon the ambient temperature which affects the resistance Ra in equations (6) and (14).

The ambient temperature could be measured with a thermometer but is more conveniently measured using the voltage V_T at the top of the bridge circuit as shown in Figure 6. The resistance of the ambient temperature measuring resistor Ra can be determined assuming that the bridge circuit is balanced using ($V_{R1} = V_{R2}$) in either of the following equations:

$$(15) \dots Ra = R2 (V_T - V_{R1})/V_{R1} \quad \text{when R3 is by-passed}$$

$$(16) \dots Ra = (R2 + R3) (V_T - V_{R1})/V_{R1} \quad \text{when R3 is not by-passed}$$

The temperature T of ambient temperature sensing resistor Ra and thus the ambient temperature can then be found using equation (4).

Any variation in ambient temperature can thus be monitored and the corresponding adjustment of the temperature to which the thermal conductivity measuring resistor Rm is heated can be determined. A suitable proportionality constant z corresponding to the temperature to which Rm is heated can then be selected to ensure the provision of precise thermal conductivity measurements despite the variation in ambient temperature. The appropriate proportionality constant z is preferably looked up in a look-up table

containing a proportionality constant z for each temperature at which the thermal conductivity measuring resistors R_m can be operated for the sensor being used.

Alternatively the values of the ratio of R_1/R_2 or $R_1/(R_2 + R_3)$ could be adjustable by at least one of R_1 and R_2 being variable to ensure that R_m is heated to a predetermined temperature. Alternatively additional resistors could be arranged to be able to be placed in series or parallel with at least one of R_1 and R_2 to adjust the ratio of R_1/R_2 or $R_1/(R_2 + R_3)$ to ensure that R_m is heated to a predetermined temperature.

Figure 7 shows the sequence of operations for controlling a sensor to determine the thermal conductivity of a gas at two temperatures. The numbered steps have the following meaning:

- 100 Start
- 101 Control transistor 60 to by-pass resistor R_3
- 102 Set counter to 0
- 103 Control V_T such that $V_{R1} = V_{R2}$
- 104 Measure V_{R1}
- 105 Measure V_T
- 106 Determine R_a using equation 15 or 16 as appropriate.
- 107 Determine ambient temperature using equation (4) from which the temperature to which R_m is heated can be determined.
- 108 Select proportionality constant z eg from a look-up table for temperature to which R_m is heated.
- 109 Calculate thermal conductivity of gas from equation (13).
- 110 Increment counter
- 111 Counter = 2?
- 112 If no: Control transistor 60 to include resistor R_3 and go to step 103.

113 If yes: Stop.

If desired step 108 could read:

"Adjust ratio of $R1/R2$ or $R1/(R2 + R3)$ as appropriate". This adjustment could be achieved by any of the methods described earlier to heat thermal conductivity measuring resistor R_m to a predetermined temperature.

Figure 8 shows the output voltage V_{RI} of the sensor 51 as a function of the temperature T of the thermal conductivity measuring resistor R_m for a fixed gas composition, ambient temperature and pressure. The sensor characteristic is found to follow an almost linear profile above a null point 200 whilst below the null point it is found to fall off sharply. From a comparison of experimental thermal conductivity results for a sample of fuel gas against theoretical calculated values, a good correlation resulted for values at temperatures above the null point and an increasingly poor correlation resulted below the null point. This may be due to thermal factors other than thermal conductivity such as convection and radiation increasingly dominating the performance of the sensor below the null point. However, above the null point even though these effects are still present, thermal conductivity dominates enabling precise thermal conductivity measurements to be achieved. For fuel gas the null point was found to be approximately 40°C. Thus thermal conductivity measuring resistor R_m is preferably operated above the null point 200 for a particular gas so that far more precise results are obtained.

To obtain the 80°C above ambient heating of R_m when $R3$ is by-passed in arm 56 of the bridge circuit, $R1$ and $R2$ are each selected to be 249Ω. To obtain the 60°C above ambient heating of R_m when $R3$ is in series with $R2$ in arm 56 of the bridge circuit, $R3$ is selected to be 20Ω.

It has been found that manufacturing variations in the values of the resistances of R_m and R_a in the sensor (generally worse than 5%) can cause the thermal conductivity measuring resistor R_m to operate at an unexpected or undesirable temperature. This could cause the thermal conductivity measuring resistor R_m to possibly operate below the null point and provide inaccurate thermal conductivity results.

To overcome the problems caused by the variability of the sensor resistances two additional electrical paths, each parallel to arm 56 of the bridge circuit between V_{R2} and earth are preferably included, each path containing a resistor. Each path is selectively opened or closed preferably by the application of an appropriate control signal to a transistor in the path. Closing one electrical path whilst $R3$ is omitted from arm 56 of the bridge circuit introduces a resistor in parallel with resistor $R2$ of arm 56 elevating the temperature to which R_m is heated. Closing the other electrical path whilst $R3$ is included in arm 56 of the bridge circuit reduces the difference between the two temperatures to which R_m is elevated. The use of the additional paths prevents the heated temperature of R_m falling to undesirable levels which may be due to resistor tolerance of R_m and R_a . These additional electrical paths can also be used to ensure that R_m is heated to a predetermined temperature despite variations in ambient temperature as described earlier.

Many modifications of the above thermal conductivity sensor could be made. For example by the use of at least one of the controlled inclusion and exclusion of any number of resistors in series or the use of a variable resistor or the inclusion of resistors in parallel in an arm of the bridge circuit, the thermal conductivity measuring resistor R_m can be heated to a corresponding number of temperatures at which the thermal conductivity can be measured. Furthermore the control circuit 53 may include any suitable electrical elements instead of resistors.

Appendix

$$\begin{aligned}
 R_m &= R_{mo} (1 + \alpha T_m) \\
 \text{and } T_m &= T_a + \theta \\
 R_m &= R_{mo} (1 + \alpha T_a + \alpha \theta) \\
 R_m &= R_{mo} + R_{mo} \alpha T_a + R_{mo} \alpha \theta \\
 \theta &= (R_m / R_{mo} \alpha) - 1/\alpha - T_a \\
 &= [R_{ao} (1 + \alpha T_a) / R_{mo} \alpha] - 1/\alpha - T_a \\
 &= [R_{ao} (1 + \alpha T_a) - R_{mo} - R_{mo} \alpha T_a] / R_{mo} \alpha \\
 &= [R_{ao} (1 + \alpha T_a) - R_{mo} (1 + \alpha T_a)] / R_{mo} \alpha \\
 \theta &= (R_{ao} - R_{mo}) (1 + \alpha T_a) / R_{mo} \alpha \\
 k &= \Psi P / \theta \\
 k &= \frac{\Psi V_{RI}^2 R_{ao} (1 + \alpha T_a) \alpha R_{mo}}{R_{RI}^2 (R_{ao} - R_{mo}) (1 + \alpha T_a)} \\
 k &= \Psi V_{RI}^2 \alpha R_{ao} R_{mo} / R_{RI}^2 (R_{ao} - R_{mo})
 \end{aligned}$$

CLAIMS

1. An apparatus for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas, the apparatus comprising means to measure the thermal conductivity of the mixture at two different temperatures and control means to infer the proportion of at least one of the components of the mixture from the thermal conductivity measurements.
2. An apparatus according to claim 1, including means to measure the temperature of the mixture and the control means being arranged to infer the proportion of at least one of the components of the mixture from the thermal conductivity measurements and the temperature measurement.
3. An apparatus according to claim 2, including means to measure the absolute pressure of the mixture and the control means being arranged to infer the proportion of at least one of the components of the mixture from the thermal conductivity measurements, the temperature measurement and the absolute pressure measurement.
4. An apparatus according to claim 3, wherein the control means is arranged to infer the proportion of at least one of the components of a mixture using the following expression:

$$X = uP + vT + wT^2 + xThC(St) + yThC(R) + z$$

where

X is inferred proportion of at least one of the components of a mixture;

P is absolute pressure of a mixture;

T is the temperature of a mixture;

ThC(St) is the thermal conductivity of a mixture at a first temperature;

ThC(R) is the thermal conductivity of a mixture at a second temperature;

and u, v, w, x, y and z are constants.

5. An apparatus according to claim 4, wherein

X is the inferred methane percentage;

P is measured in units of bar A;

T is measured in degrees Celsius

Thermal conductivity is measured in Watts/metre x Kelvin and the constants u - z have substantially the following values:

$$u = -0.44$$

$$v = -0.39$$

$$w = 0.0017$$

$$x = 41$$

$$y = -42 \text{ and}$$

$$z = -181$$

6. An apparatus according to claim 4, wherein

X is the inferred ethane/methane ratio;

P is measured in units of bar A;

T is measured in degrees Celsius;

Thermal conductivity is measured in Watts/metre x Kelvin and the constants u - z have substantially the following values:

$$u = 0.0053$$

$$v = 0.0051$$

$$w = -0.000024$$

$$x = -0.61$$

$$y = 0.66 \text{ and}$$

$$z = 3.14$$

7. An apparatus according to any of the preceding claims, wherein the means to measure the thermal conductivity of the mixture at two different temperatures includes a resistor arranged to be exposed to the mixture, means to heat the resistors to two different substantially predetermined temperatures by application of suitable current or voltage to the resistor and means to determine the thermal conductivity of the mixture from an electrical characteristic of the resistor at each of the predetermined temperatures to which it is heated.
8. An engine management system for an LNG fuelled engine, the system including an apparatus according to any of the preceding claims for determining the proportion of at least one of the components of LNG fuel and means to modify one or more engine parameters in response to the determined proportion of at least one of the components of LNG fuel.
9. An apparatus for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas substantially as herein before described with reference to the accompanying drawings.
10. A method of determining the proportion of at least one of the components of a fluid mixture of liquid natural gas, the method comprising measuring the thermal conductivity of the mixture at a first temperature, measuring the thermal conductivity of the fluid at a second temperature and inferring the proportion of at least one of the components of the mixture from the thermal conductivity measurements.

11. A method according to claim 10, including measuring the temperature of the mixture and inferring the proportion of at least one of the components of the mixture from the thermal conductivity measurements and the temperature measurement.
12. A method according to claim 11, including measuring the absolute pressure of the mixture and the proportion of at least one of the components of the mixture from the thermal conductivity measurements, the temperature measurement and the absolute pressure measurement.
13. A method according to claim 12, wherein the proportion of at least one of the components of a mixture is inferred using the following expression:

$$X = uP + vT + wT^2 + xThC(St) + yThC(R) + z$$
 where
 X is inferred proportion of at least one of the component of a mixture
 P is the absolute pressure of a mixture;
 T is the temperature of a mixture;
 ThC(St) is the thermal conductivity of a mixture at a first temperature;
 ThC(R) is the thermal conductivity of a mixture at a second temperature;
 and u, v, w, x, y and z are constants.
14. A method according to claim 13, wherein
 X is the inferred methane percentage;
 P is measured in units of bar A;
 T is measured in degrees Celsius
 Thermal conductivity is measured in Watts/metre x Kelvin and the constants u - z have substantially the following values:

$$u = -0.44$$

$$v = -0.39$$

$$w = 0.0017$$

$$x = 41$$

$$y = -42 \text{ and}$$

$$z = -181$$

15. A method according to claim 13, wherein

X is the inferred ethane/methane ratio;

P is measured in units of bar A;

T is measured in degrees Celsius;

Thermal conductivity is measured in Watts/metre x Kelvin and the constants u - z have substantially the following values:

$$u = 0.0053$$

$$v = 0.0051$$

$$w = -0.000024$$

$$x = -0.61$$

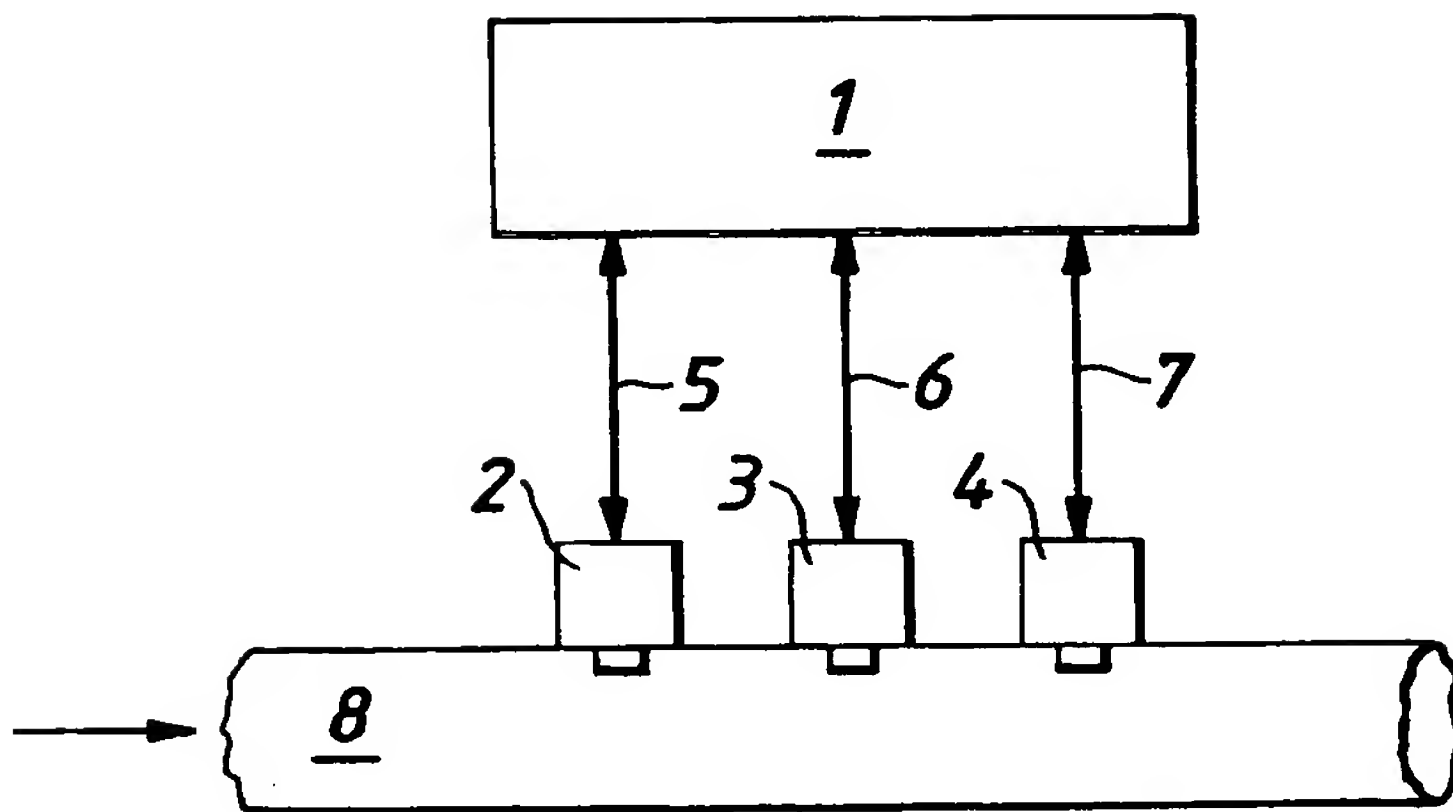
$$y = 0.66 \text{ and}$$

$$z = 3.14$$

16. A method for determining the proportion of at least one of the components of a fluid mixture of liquid natural gas substantially as herein before described with reference to the accompanying drawings.

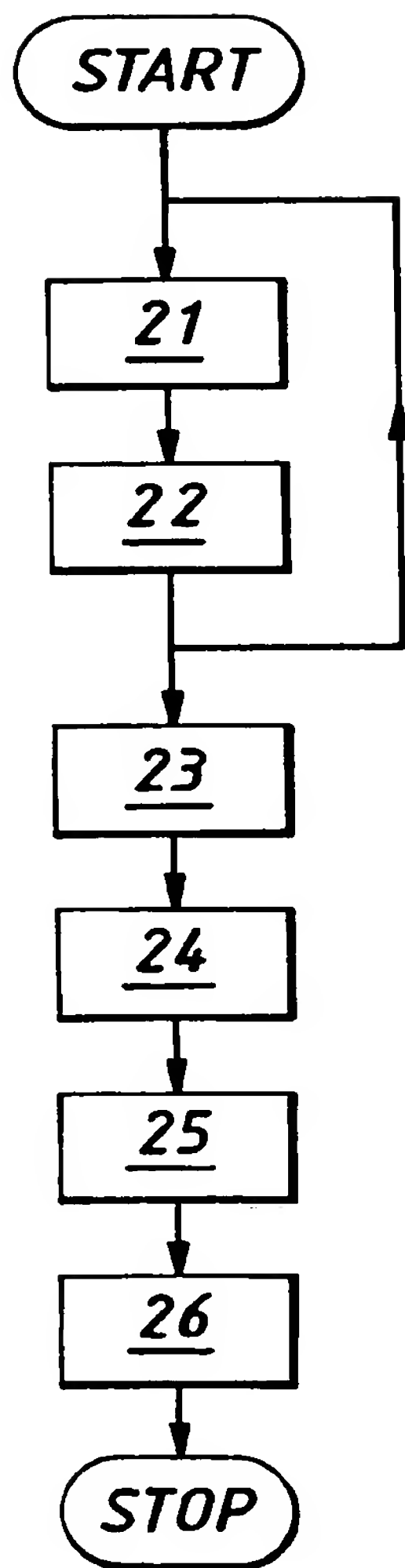
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FIG. 1.



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FIG. 2.



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FIG. 3.

Methane Inference
($2*SD = +/- 0.33\%$)

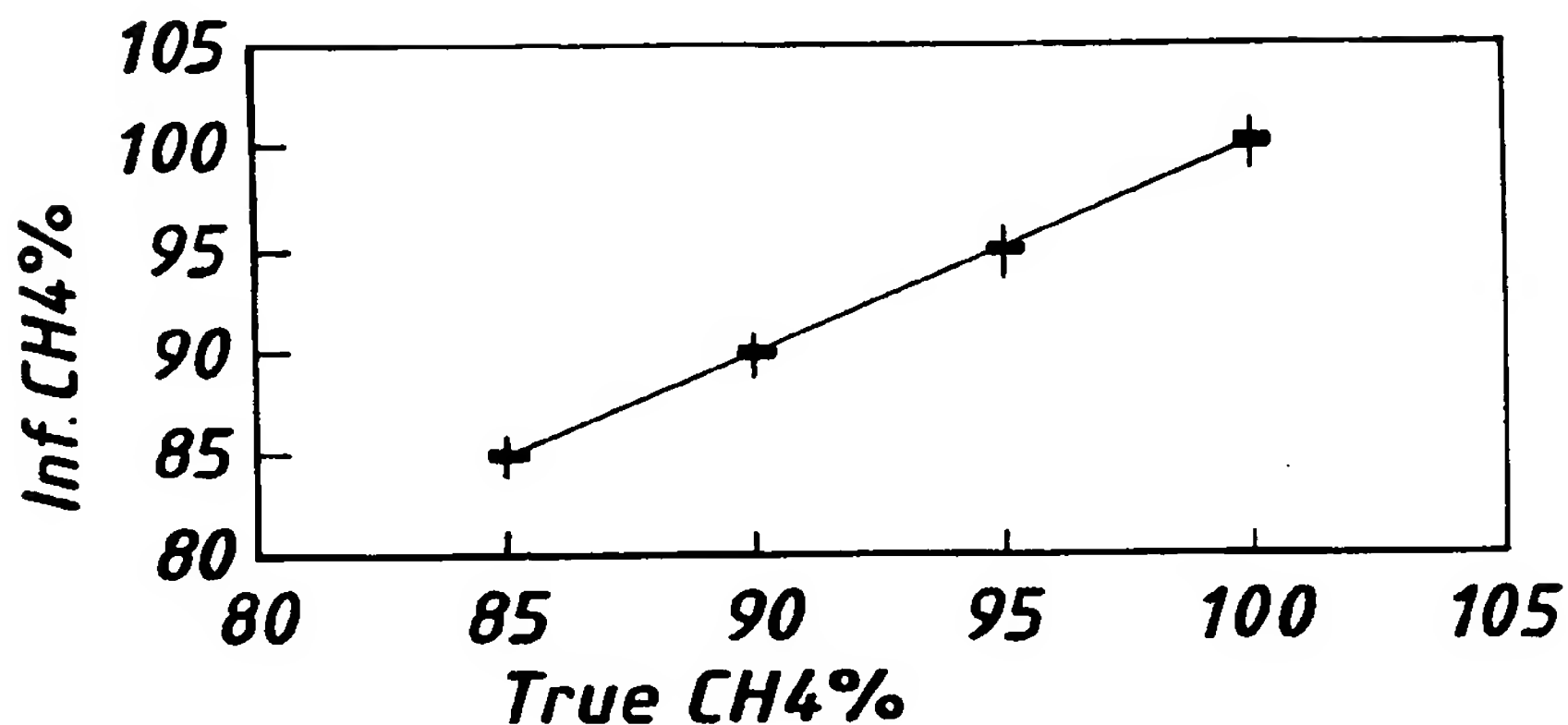
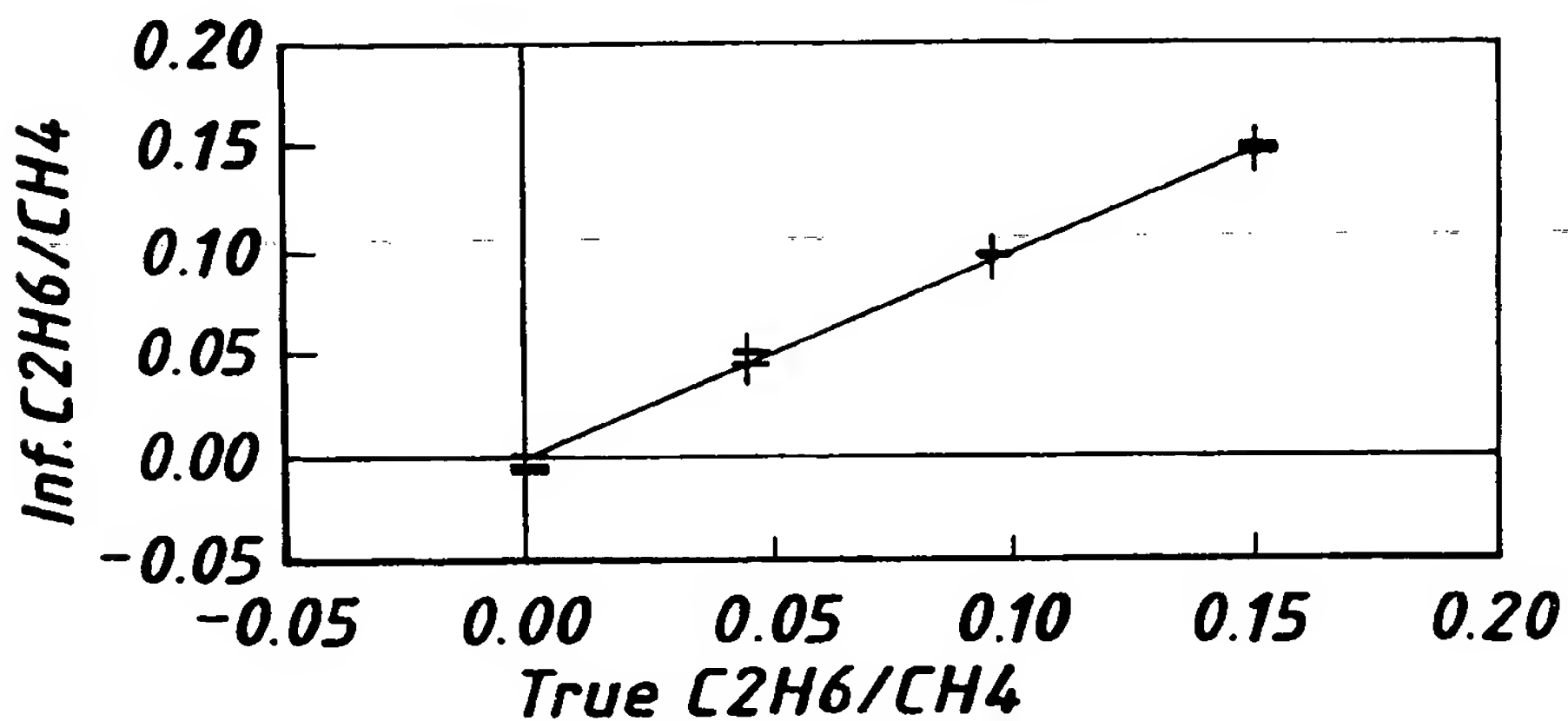


FIG. 4.

Ethane: Methane Inference
($2*SD = +/- 0.0049$)



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FIG. 5.

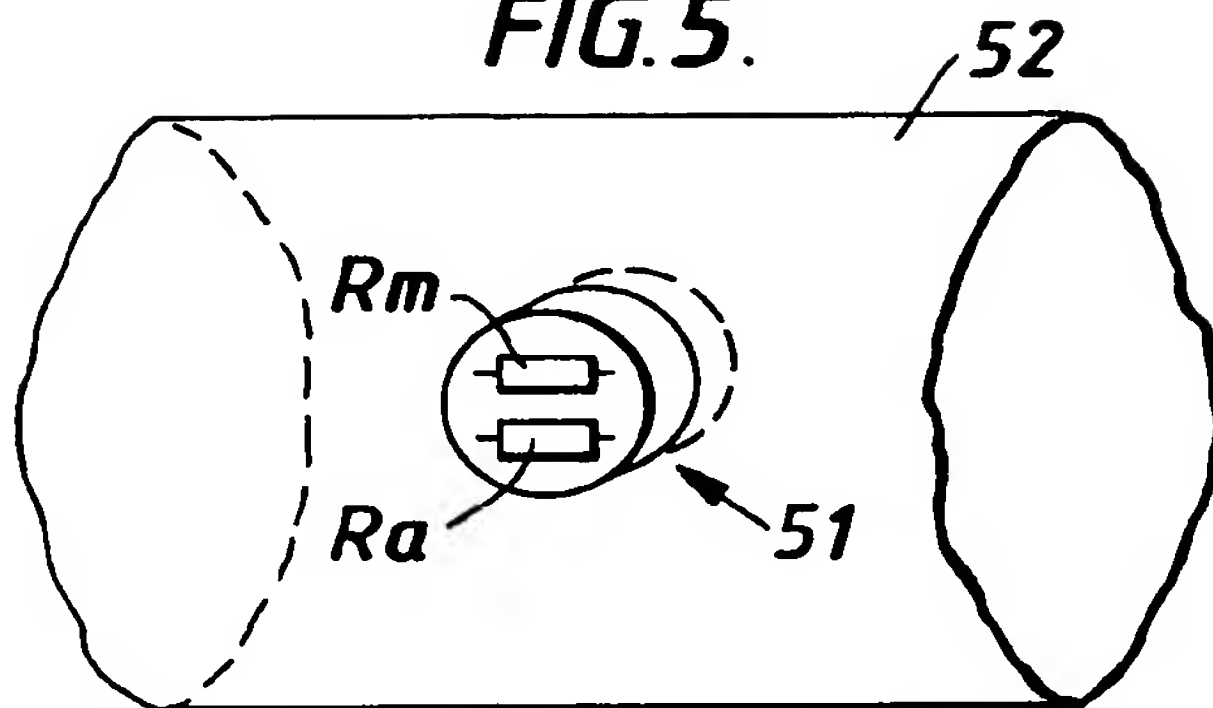
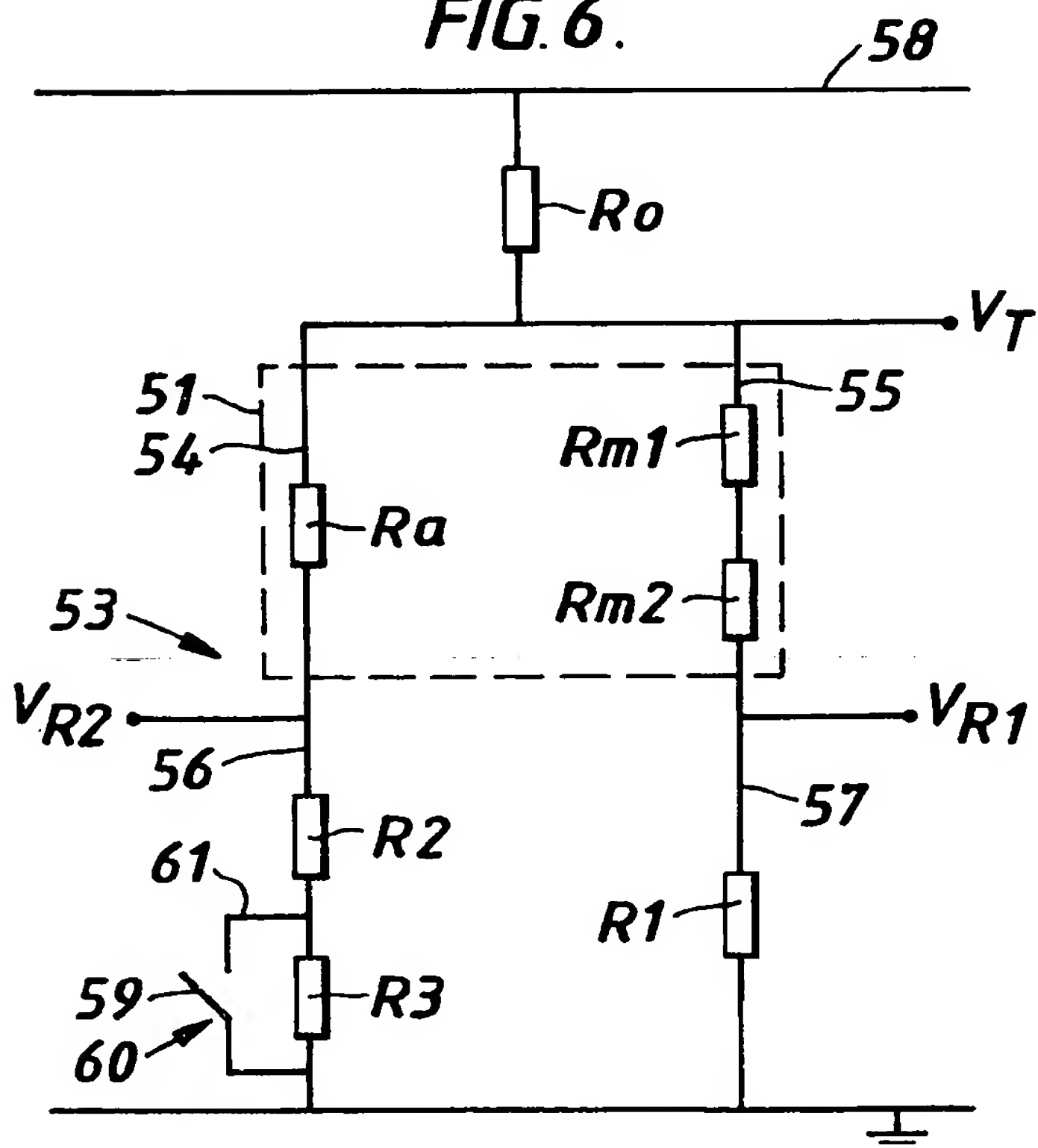


FIG. 6.



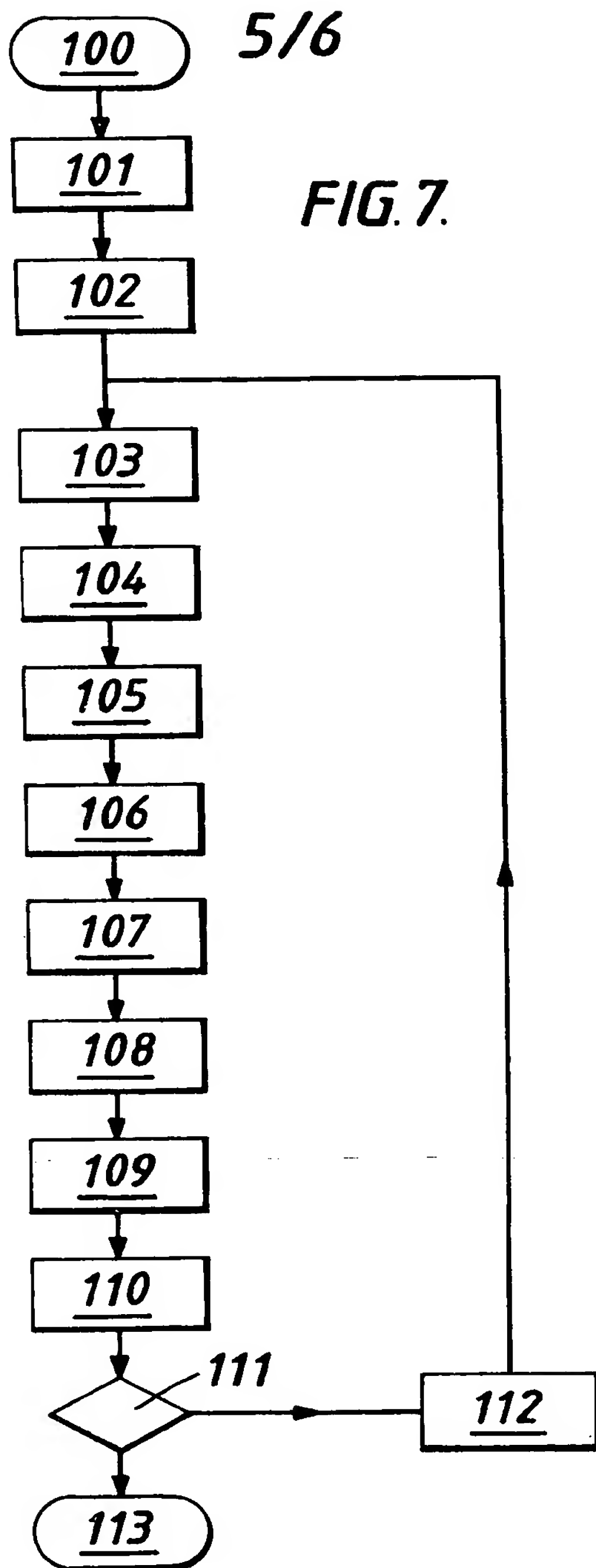
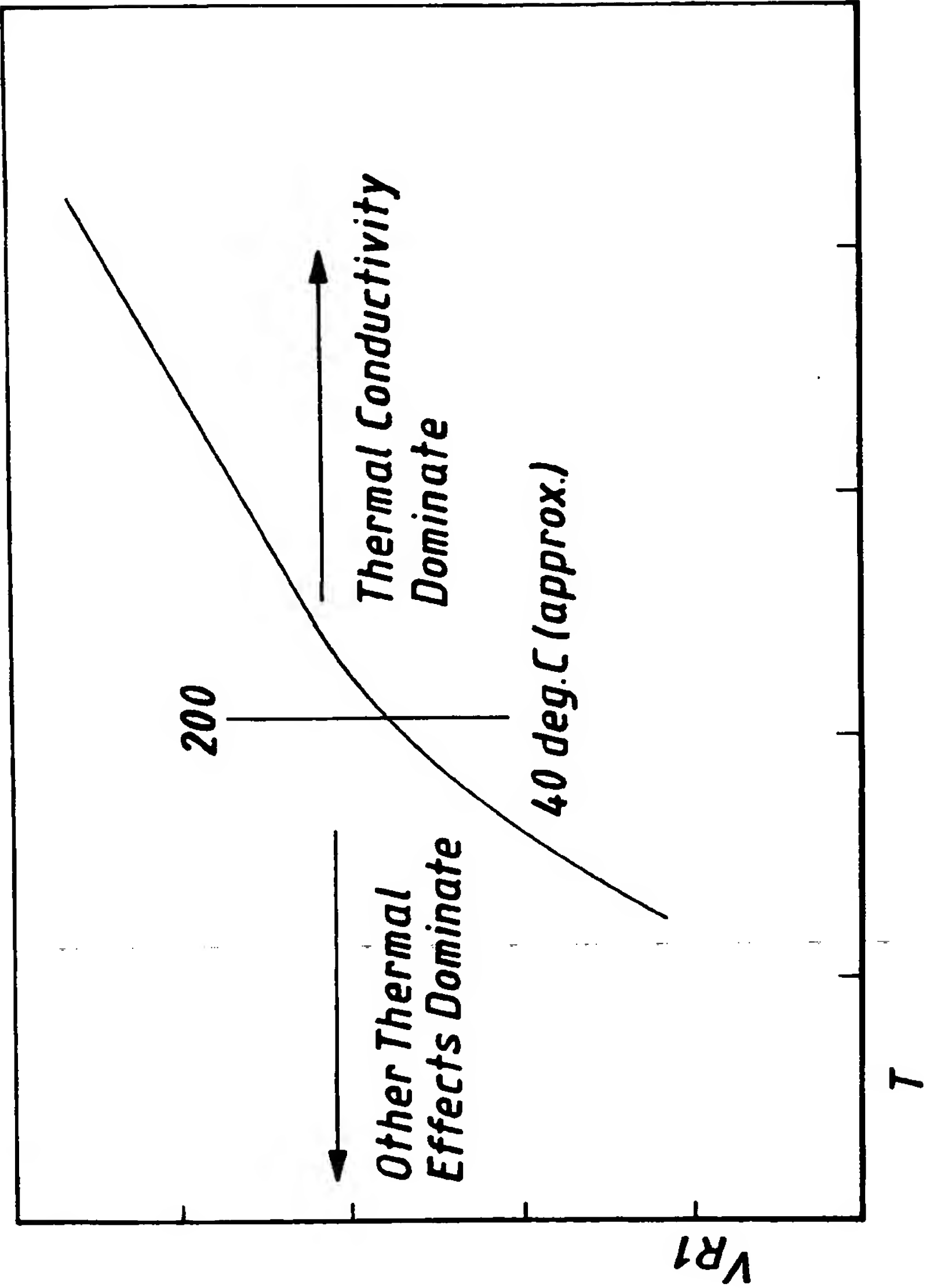


FIG. 8.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01363

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G01N33/28 G01N27/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N F02D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 902 138 A (GOELDNER HEINZ-DIETER ET AL) 20 February 1990 (1990-02-20) abstract column 1, line 41 - line 44	1,10
Y	column 2, line 20 - line 30 column 5, line 24 - line 32 column 5, line 36 - line 41 column 5, line 55 - line 67 claim 1	2,7,11
Y	US 4 804 632 A (SCHUCK HANSJOCHEN ET AL) 14 February 1989 (1989-02-14) abstract column 2, line 54 -column 3, line 10 claims 9,10	2,7,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 July 2000

Date of mailing of the international search report

08/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Angelié, E

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/GB 00/01363

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) & JP 08 050109 A (YAMATAKE HONEYWELL CO LTD), 20 February 1996 (1996-02-20) abstract claim 1	3
P,A	WO 00 11465 A (HAMMOND PAUL STEVEN ;PRICE BARRY LEONARD (GB); THURSTON ROBERT RIC) 2 March 2000 (2000-03-02) abstract page 7, line 19 -page 8, line 2 page 8, line 10 - line 17 page 8, line 23 page 9, line 1 - line 5 claims 2,3	4,13
A	US 5 353 765 A (SAIKALIS GEORGE ET AL) 11 October 1994 (1994-10-11) abstract figures 1-3 column 1, line 21 - line 37 column 1, line 51 -column 2, line 24 claims 1-4	8

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int .tional Application No

PCT/GB 00/01363

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4902138 A	20-02-1990	DE 3711511 C CN 1011917 B EP 0285833 A	30-06-1988 06-03-1991 12-10-1988
US 4804632 A	14-02-1989	GB 2185577 A DE 3635513 A DE 3777854 A EP 0234251 A	22-07-1987 23-07-1987 07-05-1992 02-09-1987
JP 08050109 A	20-02-1996	NONE	
WO 0011465 A	02-03-2000	AU 5433899 A GB 2340945 A	14-03-2000 01-03-2000
US 5353765 A	11-10-1994	DE 4415377 A JP 7071325 A	17-11-1994 14-03-1995